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Poplar from phytoremediation as a renewable energy source: gasification properties and pollution analysis

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Abstract

Biomass gasification is a very efficient process to produce clean energy in the form of a fuel gas (syngas). Hazelnut shells and poplar have good energy production potential and they are abundant in nature. Hazelnut shells have the characteristics of a very good fuel and poplar is among the fastest growing trees; furthermore, poplar demonstrated the capability to absorb organic contaminants (i.e. heavy metals) from the soil in which they are cultivated. However, poplar is not usually used for biomass gasification and its potential is not fully assessed. Here, 3 types of biomass, hazelnut shells (HS), simple poplar (P) and poplar coming from a phytoremediation procedure (PHYP), were chosen as representative samples to be characterized and tested in a steam gasification process carried out on a bench scale fluidized bed gasifier. A comparison is reported on gasification results, such as gas composition, tar production and gas yield for the biomass feedstocks mentioned above. It was concluded that hazelnut shells and poplar (P and PHYP) could be easily gasified in a fluidized bed gasifier, thus producing a good quality gas with low polluting by-products. The PHYP sample showed lower tar content and higher gas yield. It is guessed that Ca and Mg, found in higher quantities in the PHYP sample, could have had a catalytic effect in tar reforming thus producing lower quantity of heavy hydrocarbons.

Keywords: biomass gasification, fluidized bed gasifier, hazelnut shell, poplar, phytoremediation, heavy metals, alkali metals

Nomenclature

XRF	X-ray fluorescence analysis

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GC	Gas-cromatograph
GC-MS	Gas-chromatograph with mass spectrometer
HS	Hazelnut shells
P	Poplar Pruning
PHYP	Poplar used in Phytoremediation Pruning
AAEM	Alkali and Alkaline Earth Metals

1. Introduction

The continuous growing demand of electricity and transportation fuels, along with harmful effects of using fossil fuels regarding the emissions and the green house effect, has assured a viable future for the development of alternative fuels from renewable sources such as biomass.
Biomass is a renewable, carbon neutral energy source and biomass technologies, if properly developed and improved, could be used in the future as substitute of fossil fuels, promoting environmental and social benefits. [1][2][3][4]
Biomass is the fourth major source of primary energy uses following coal, petroleum and natural gas [5]. The simplest utilization of biomass is to burn it to produce heat. This use is largely practiced in developing countries; it can be a way for waste reduction but if not properly controlled it can release pollutants for the health and the environment furthermore it is not effective in producing higher quality fuels or electrical power.
Bio-chemical processes like bio-methanation and thermo-chemical methods such as combustion (fixed amount of air/oxygen provided to the process), pyrolysis and gasification are used in recovering energy from biomass. Biomass gasification is one of such promising technologies. [6][7] The gasification of biomass and the subsequent conversion to electric power, heat, or synthetic natural gas (SNG) offers the possibility to produce different products in one process under minimizing potential losses in the so-called poly-generation approach. Due to these advantages, biomass gasification technology has drawn an attention around the world and stands out among other renewable energy conversion systems which mostly suffer from stochastic behaviour of the source and lead to some serious grid connection issues. Biomass based energy has been prioritized in European Union (EU) strategies mainly based on Kyoto protocol and recent Paris agreement to mitigate climate change and improve energy security [8].
According to the Paris agreement in 2015, the member states of the EU are committed to produce 20% of their energy demands from renewable sources, including biomass, by the year 2020. In such context, biomass gasification research and development work has increased to improve efficiency and reduce pollutants.
Furthermore, in recent years a novel bonification technology called phytoremediation was developed and tested. This approach is based on the plantation of trees that are able to extract pollutants from the contaminated soil. In an ongoing project, carried out by IRSA CNR and IBAF CNR institutes, a poplar clone (Pioppo Monviso) was planted in a region close to Taranto, Southern Italy, that was polluted by PCBs (Polychlorinated biphenyl) and heavy metals [9]. A specific objective of such research deals with the investigation of the capabilities of contaminated poplar as a feedstock for biomass gasification together with the characterisation of the dispersion of heavy metals and/or PCB during the process. The final aim of the research project is to certify a gasification process able to produce syngas free from contaminant to be classified as renewable energy source.
In this work the results of characterization and gasification tests of ligno-cellulosic feedstocks, namely hazelnut shells and two samples of hybrid-poplar, are presented. The tests were carried out in a bench scale fluidized bed gasifier in the DIMA laboratory of the Sapienza University of Rome. This type of gasifier is chosen in this work because its advantages in term of homogeneous temperature distribution in the bed (typically temperature ranges between 700-900 °C) as well the high residence time of the fuel in the reactor [10].
Hazelnut shells are chosen as a reference fuel because of their abundance and their good physic-chemical characteristics (low moisture and ash content); simple hybrid-poplar is chosen because it's among the fastest growing temperate trees in the world that can be harvested up to few times a year and also have a very high capacity of absorbing both organic and non-organic pollutants from the environment: for this reason a sample of poplar grown in a contaminated valley was also used in the tests for the comparison with the other two fuels.
The properties of these two feedstocks are compared with the "contaminated" poplar coming from the contaminated soil in Taranto cited before [9].
The three biomass samples are thus analysed from the physic-chemical point of view, by means of the main characterization methods, and then tested in a gasification reactor to investigate the gas composition and tar content. From these comparisons, it will be possible to deduce the characteristics of the different kinds of biomass, hazelnut

and poplar, and furthermore to analyse the possible variations of results of the poplar used in the phytoremediation procedure.

2. Experimental

2.1. Feedstock characterization

The biomass feedstocks used in this study, hazelnut shells (HS), hybrid poplar pruning (P), and pruning of hybrid poplar used in phytoremediation (PHYP), have been pre-treated before being used in the bench scale gasification reactor. Firstly, the biomass has been dried, to reduce its humidity content; subsequently it was chopped and sieved to reduce its granulometry between 1 and 2 mm. These pre-treatments are necessary for the requirements of the bench scale gasifier and for its feeding system. In fact, it is important to feed dry biomass to the reactor, to bring all the samples at the same initial conditions; furthermore, a small granulometry of the biomass is needed, to avoid the blocking of the bench scale feeding system.

The biomass feedstocks have been characterized before their use in the gasification reactor. The carried out analysis referred to: humidity, to calculate the water content in the biomass as received; CHNS analysis, to evaluate the content of C, H, N and S; elemental analysis by means of XRF, to obtain the quantity of the metals and alkali metals possibly contained in the biomass.

2.2. Experimental setup

The gasification tests have been carried out in a bench scale fluidized bed gasifier, in the DIMA Laboratory of Sapienza University of Rome.

The experimental setup, shown in Figure 1, is mainly composed by a screw feeding system for the biomass, a bench scale fluidized bed gasifier, gas and steam supply systems, systems for the removal of the particulate from the gas, a gas cooling system and metering and analysing systems for the gas produced.

The gasifier is filled with olivine sand (bed material), that is fluidized by the flows of gasification agents (air and steam) sent from the bottom of the reactor. The bed material, once in fluidization regime, behaves like a bubbling liquid and assures an optimal mixing, homogeneity of the gas composition, and thermal inertia.

The feedstock is fed to the top of the reactor by the screw feeding system that assures a continuous flow of biomass inside the reactor.

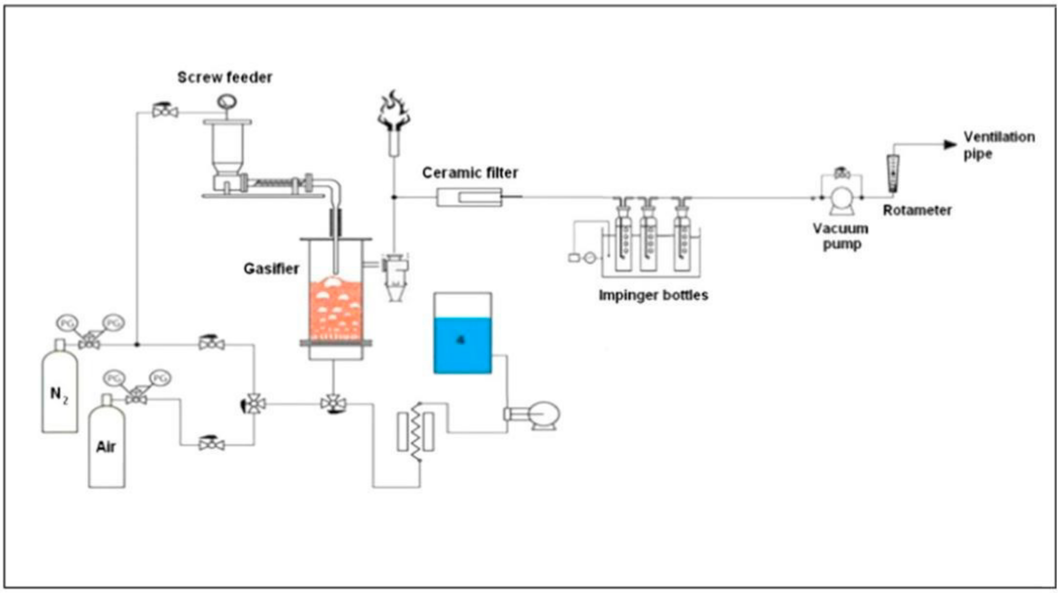

Figure 1 - Scheme of the bench scale gasification plant

For the execution of a gasification test, the reactor is placed in an electric furnace with PID control to maintain the temperature of bed at a the desired temperature of 800°C; the gasification agents are preheated to the temperature of 450°C in the wind-box of the gasifier in which air and steam are mixed before entering the reactor. [10]

The gas produced, mainly composed of H_2, CO, CO_2, CH_4, as wells as particulate and heavy hydrocarbons, flows out of the reactor where it is cleaned before the analysis. Firstly, the gas passes through the particulate removal units: a cyclone to remove the coarse particulate, and a ceramic filter to remove very fine particulate. After, the gas goes to the sampling system, consisting in a series of impinger bottles filled with 2-propanol, immersed in a cold bath kept at -10°C. Water and tars condense in the cold traps (i.e. the impinger bottles). Tars are later collected for the analysis, while the clean gas goes finally to the GC, for the analysis of the gas composition. The content of the impinger bottles are analysed by means of a GC-MS for the identification and quantification of the tar compounds, and eventual heavy metals or PCBs, contained in the gas flow.

The gas is moved through all the circuit by means of a vacuum pump; its flow is measured and controlled by a mass-flow controller.

3. Results and discussion

3.1. Characterization results

The biomass feedstocks were preliminary analysed to determine their physic-chemical properties. The characterization analysis was carried out according to the European standards. The moisture content was measured following the standard UNI EN 1447-2, using a drying oven and an analytic balance; the ash content was obtained according to the standard UNI EN 14775, using a muffle furnace and an analytic balance; the content of CHNS was determined following the standard UNI EN 15104, using an elemental analyzer and an analytic balance. The values of HHV and LHV were calculated starting from the data obtained in the previous analysis.

Table 1 shows the characterization results for the samples HS, P and PHYP.

Table 1 - Characterization analysis of the 3 biomass samples: HS, P and PHYP

	HS	P	PHYP
Moisture (%)	9.44	7.2	4.47
Ash (%)	1.45	3.04	5.81
C (%)	48.30	46.00	47.76
H (%)	6.25	5.86	6.14
N (%)	1.50	0.16	1.92
S (%)	0.83	0.85	0.86
O (%)	41.67	44.08	37.51
HHV (MJ/kg)	19.94	18.42	19.96
LHV (MJ/kg)	17.83	16.92	18.96

From the results displayed in Table 1 it is possible to notice that the sample HS has a high content in C and a very low ash content; these characteristics confirms the high quality of hazelnut shells as biomass fuel, that indeed show also a high LHV. The P sample also shows good qualities but lower C content and higher ash content, when compared with the HS sample. The PHYP sample shows very low moisture, and a high LHV; PHYP shows also higher ash content compared to the other samples, maybe related to its use in contaminated soils.

The samples HS, P and PHYP have also been analyzed in order to obtain the possible content of alkali and heavy metals. PHYP, since used in a process of phytoremediation, is expected to contain a higher quantity of heavy metals. The XRF analysis was performed on the biomass feedstocks, in order to show the content of all the elements with MW higher than Na. The elements found in relevant quantities are shown in **Error! Reference source not found.**.

From the values presented in Table 2, it is possible to observe that, for what concerns alkali metals, PHYP shows higher quantities of Ca and Mg compared to the other biomass samples. Ca is more than 3 times higher in PHYP with respect to the other samples; Mg is approximately 5 times higher in PHYP than in HS and P. This can be related to the soil contents in CaCO3 and Mg compounds.

Table 2 - Alkali and heavy metals contents in the biomass samples analysed (HS, P, PHYP)

	HS	P	PHYP
		Alkali metals (%)	
Na	0.088	0.172	0.146
K	0.569	0.364	0.517
Ca	0.318	0.508	1.805
Mg	0.032	0.029	0.150
		Heavy metals (ppm_w)	
Cu	23.6	2.6	2.9
Cd	0.5	0.4	0.4
Ni	25.0	70.4	35.4
Pb	1.1	0.1	1.0
Zn	8.3	30.3	64.7
Hg	1.0	1.0	1.0
As	0.1	0.6	0.7
Mn	43.5	1.0	2.3
Sr	52.1	30.3	309.6

Heavy metals are found in very low quantities in each of the 3 samples; exceptions are represented by Zn and Sr that are found in higher quantities in the PHYP sample. Sr is 10 times higher in PHYP than in P, and Zn is approximately 2 times higher in PHYP than in P.

The higher content of the mentioned heavy metals could be related to the contaminated soil in which the PHYP plants were grown for the experimentation on the phytoremediation method.

PCBs were extracted from plant and soil samples with an Accelerated Solvent Extractor (ASE 300 DIONEX) and then analyses were performed by gas chromatography (GC) with a mass spectrometric detector. It is interesting to note that, also if the soil is highly contaminated by PCBs, only few traces of PCB (1,629 ng/g, dev st= 0,05) were found in the biomass.

3.2. Gasification results

The gasification performance is mainly evaluated on the basis of gas composition and gas yield. Furthermore, the tars are also analyzed and quantified. In all the tests here presented, test conditions are maintained in a fixed range as reported in Table 3:

Table 3 - Operating conditions used in the biomass gasification tests

T (°C)	Air (Nml/min)	H_2O (g/h)	Biomass (g/h)	Steam/Biomass	E.R.
800~820	4440~5900	120~150	250~300	0.4~0.5	0.3

As it can be seen in Figure 2, the composition of the syngas from hazelnut shells, simple poplar and phytoremediation poplar show a very similar trend. The results obtained here agree fairly well with previous studies, in terms of hydrogen and methane production [12].

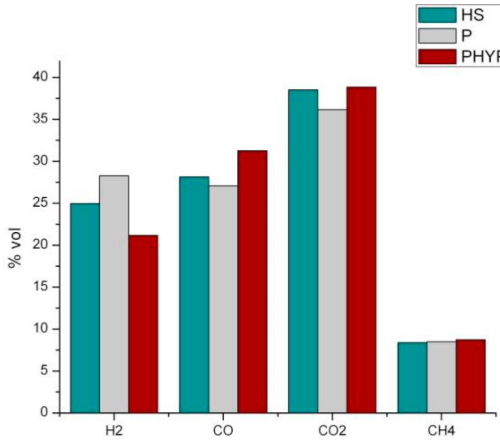

Figure 2 – Gas composition (% vol nitrogen free) obtained during gasification tests of HS, P and PHYP

During the gasification tests, downstream from the reactor the syngas passed through cold traps filled with 2-propanol for the condensation and further analysis of the heavy hydrocarbons in the syngas. In the analysis of tar only three main tars (toluene, naphthalene and phenol) are considered, since the other tar compounds are found in negligible quantities. The results are shown in Figure 3.

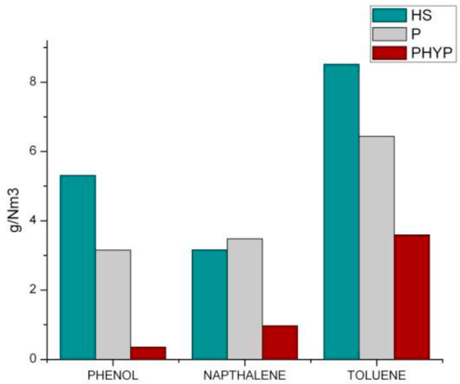

Figure 3 – Main tar compounds produced in the gasification tests of HS, P and PHYP

The simple poplar and hazelnut shells show similar tar results with little discrepancy; but the PHYP yields noticeably less heavy hydrocarbons, compared to the other samples. The explanation for this result could be found in the higher concentration of Ca and Mg found in the PHYP, as can be seen in Table 2; it is argued that Ca and Mg had a catalytic effect on tars reforming, leading to a lower content of heavy hydrocarbons in the gas. Since the PHYP has been cultivated in lands with alkaline properties (pH close to 8, [9]) it is guessed that alkali and alkaline earth metals (AAEM) are present in the soil. Therefore, in the phytoremediation process the PHYP has absorbed them through the roots.

It is well-known that AAEM species can be good catalysts for the combustion/gasification and can lead to higher carbon conversion, tar reforming and higher gas yield [13] [14]. In the experiments here carried out, Ca and Mg could have worked as primary catalysts in the fluidized bed reactor and leading to a relevantly lower amount of heavy hydrocarbons in the syngas.

The gas yields of the different samples have also been analyzed for the comparison of the gasification results on the 3 biomass feedstocks.

Depending on the feedstock characteristics, such as volatile organic dry matter content, as well as microbial degradability of the material, biomass gasification shows a specific syngas yield and composition for certain groups of feedstocks. Due to the similar characteristics of HS, P and PHYP, it was expected to obtain similar values of gas yield. P and HS gasification shows similar values of gas yield, as reported in Table 4. In PHYP case the syngas yield is higher than simple poplar and hazelnut shells, of 38% and 15% respectively. This result could be again related to the higher content of Ca and Mg in PHYP, that could have played a catalytic role in tar reforming and contributed to the formation of further syngas that increased the value of gas yield.

Table 4 – Gas yield for the samples HS, P, PHYP (nitrogen free)

	Gas yield (Nm3/kg)
PHYP	1.27
P	0.92
HS	1.10

4. Conclusions

A series of experimental tests on the fluidized bed bench scale gasifier have been performed with both air and steam as gasification agents in order to compare the gas composition, tar analysis and gas yield of three different biomass samples (P, PHYP, HS).

The gas composition was very similar for the 3 biomass samples: $H_2 \sim 25\%$, $CO \sim 28\%$, $CO_2 \sim 38\%$ and $CH_4 \sim 8\%$. As for the heavy hydrocarbons produced during the gasification, it has been observed that PHYP has the lowest tar content if compared to the other biomass samples. In detail, for all the compounds analyzed, toluene, naphthalene and phenol, the tar content in PHYP was about half of the content in HS and P.

It is possible to interpret this result making reference to XRF analysis of the samples: PHYP showed the highest content in Ca and Mg. The presence of AAEM in the biomass, possibly absorbed by the PHYP from the contaminated soil, played a catalytic role in tar reforming directly inside the gasification reactor, resulting in a lower amount of heavy hydrocarbons with respect to P and HS. The hypothesis could be confirmed by the values of gas yield for the 3 samples; PHYP showed a superior value that could be ascribed to the surplus of gas produced from the higher grade of tar reforming.

As a final item, it is important to remark that one of the main objective of the ongoing research is to demonstrate the capability of PHYP to be used as a phyto-remediation tool as well as a renewable energy source. To this end, we point out that in the several samples we examined (coming from the poplar trunks and branches), the presence of heavy metals and PCBs was almost negligible, being the metals concentrated in the roots. This suggests that such class of biomass can be treated as renewable sources.

The problems related to the presence of some heavy metal elements in PHYP and the fate of these metals distributed in the different parts of the gasifier plant, are left for future studies when poplar roots will be available also.

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References

[1] E. Bocci, A. Di Carlo, L. Vecchione, M. Villarini, M. De Falco, and A. Dell'Era, "Technical economic analysis of an innovative cogenerative small scale biomass gasification power plant," *Comput. Sci. its Appl.*, 2013.

[2] A. V. Bridgwater, "The technical and economic feasibility of biomass gasification for power generation," *Fuel*, vol. 74, no. 5, pp. 631–653, 1995.

[3] R. Amirante and P. Tamburrano, "Novel , cost-effective configurations of combined power plants for small-scale cogeneration from biomass : Feasibility study and performance optimization," *Energy Convers. Manag.*, vol. 97, pp. 111–120, 2015.

[4] D. Borello, B. De Caprariis, P. De Filippis, A. Di Carlo, A. Marchegiani, A. M. Pantaleo, N. Shah, and P. Venturini, "Thermo-Economic Assessment of a Olive Pomace Gasifier for Cogeneration Applications," *Energy Procedia*, vol. 75, pp. 252–258, 2015.

[5] K. Kwant and P. Buckley, "IEA BioEnergy: Annual Report 2015," 2015.

[6] E. Bocci, M. Sisinni, M. Moneti, L. Vecchione, A. Di Carlo, and M. Villarini, "State of Art of Small Scale Biomass Gasification Power Systems: A Review of the Different Typologies," *Energy Procedia*, vol. 45, pp. 247–256, 2014.

[7] H. Boerrigter and R. Rauch, "Review of applications of gases from biomass gasification," *ECN Biomass, Coal Environ. …*, no. June, p. 33, 2006.

[8] D. Wei, E. Cameron, S. Harris, E. Prattico, G. Scheerder, and J. Zhou, "The Paris Agreement - What It Means for Business," 2016.

[9] V. Ancona, A. Barra Caracciolo, P. Grenni, M. Di Lenola, C. Campanale, A. Calabrese, V.F. Uricchio, G. Mascolo, M. Massacci, Plant-assisted bioremediation of a historically PCB and heavy metal-contaminated area in Southern Italy, New Biotechnol. (2016), http://dx.doi.org/10.1016/j.nbt.2016.09.006.

[10] A. Di Carlo, D. Borello, M. Sisinni, E. Savuto, P. Venturini, E. Bocci, and K. Kuramoto, "Reforming of tar contained in a raw fuel gas from biomass gasification using nickel-mayenite catalyst," *Int. J. Hydrogen Energy*, vol. 40, no. 30, pp. 9088–9095, 2015.

[11] M. Šyc, M. Pohořelý, M. Jeremiáš, M. Vosecký, P. Kameníková, S. Skoblia, K. Svoboda, and M. Punčochář, "Behavior of heavy metals in steam fluidized bed gasification of contaminated biomass," *Energy and Fuels*, vol. 25, no. 5, pp. 2284–2291, 2011.

[12] D. L. Carpenter, C. J. Feik, K. X. Gaston, W. Jablonski, R. L. Bain, S. D. Phillips, and M. R. Nimlos, "Pilot-scale gasification of corn stover, wood, switchgrass, and wheat straw," *Ind. Eng. Chem. Res.*, vol. 49, pp. 1859–1871, 2010.

[13] K. Yip, F. Tian, J. I. Hayashi, and H. Wu, "Effect of alkali and alkaline earth metallic species on biochar reactivity and syngas compositions during steam gasification," *Energy and Fuels*, vol. 24, no. 1, pp. 173–181, 2010.

[14] F. Kirnbauer, V. Wilk, H. Kitzler, S. Kern, and H. Hofbauer, "The positive effects of bed material coating on tar reduction in a dual fluidized bed gasifier," *Fuel*, vol. 95, pp. 553–562, 2012.